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USE OF NONFERROUS METAL ORE CONCENTRATION WASTES IN PRODUCTION OF CERAMICS

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The possibility of using copper-nickel ore concentration wastes as a component of ceramic pastes for production of ceramic tiles was investigated. The optimum content of the wastes in the ceramic pastes and the firing conditions were determined. The physicomechanical properties of the materials obtained were investigated. It was found that copper-nickel ore concentration wastes can be used in ceramic paste compositions for making facing tiles with satisfactory properties: water absorption of 12.7 – 13.3%, flexural strength of 10.0 – 12.9 MPa, and cold resistance of more than 25 cycles.

The possibility of using natural raw material in ceramics production and the criteria for assessing its quality have been relatively well investigated. However, due to the reduction in reserves of traditional ceramic raw material, using industrial wastes, which are raw materials that do not require additional processing in many cases, is now increasingly urgent. This will allow reducing product cost and conserve traditional ceramic raw material. Important variations in the chemical and mineral compositions are a characteristic feature of most secondary raw materials. Inadequate research on the raw material itself and its behavior in pastes in heat treatment restrict its use in industry. All of this makes it necessary to conduct additional studies to determine the possibility of using secondary raw material for production of different kinds of ceramic materials.

Ore concentration wastes are represented by silicates and aluminosilicates, including magnesium, in most cases. The prospects for utilizing wastes containing magnesium silicates is determined by the features of their crystallization, capacity for isomorphism, and possibility of reciprocal transitions of aqueous and anhydrous compounds. In the ceramics industry, silicates play the basic role in formation of the performance properties of the materials obtained [1]. Wastes from concentration of copper-containing, including copper-nickel ores, are used for production of ceramic tiles [2, 3].

We report the results of studies on fabricating ceramic tiles made from copper-nickel ore concentration waste dumps (Afrikanda, Murmansk Oblast). The enormous amount of wastes accumulated at present in tailing ponds causes important environmental damage. Copper-nickel ore concentration wastes from the Pechengsk ore field, consisting of 60.0 – 90.0%[2] magnesium hydrosilicates (serpentines, talc, chlorites), to a lesser degree (0.2 – 20.0%) anhydrous magnesium silicates (olivine, pyroxenes), carbonates (calcite, dolomite), 0.1 – 5.0%, oxides (magnetite, titanomagnetite, chromite), 5.0 – 15.0%, and sulfides (primarily pyrrotine), 1.0 – 3.0%, can be considered as raw material for production of ceramic materials.

Studies on industrial processing of these wastes are complicated not only by the variety of the initial compositions but also by the processes that arise during storage and alter the phase, granulometric compositions, etc. The wastes investigated are ultradisperse materials with predominance of particles smaller than 10 μm in size, which allows using them without preliminary preparation. This is an important factor in the manufacturing process.

Copper-nickel ore concentration wastes are characterized by a high content of iron and magnesium oxides. The refractoriness of the wastes is 1250°C and the plasticity number is 5. According to the findings of thermographic analysis, several endothermic effects can be seen in the thermograms. The first one, in the 170 – 280°C range, is due to loss of low-temperature sorbed or interstitial water by hydrochlorites and mixed-lamellar minerals of the serpentine-montmorillonite type, and constitution water with chlorites and serpentines is lost at 615 – 770°C. The endothermic effect at 910 – 930°C indicates decomposition of dolomite and calcite at a temperature of approximately 950°C. In addition,

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[2] Here and below: mass content.

TABLE 1

Components	Mass content, %									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	R_2O	P_2O_5	SO_3	calcination loss
Concentration wastes	41.92	8.66	17.72	–	3.67	17.26	1.65	–	–	9.20
Clay:										
Ermakovskoe	58.80	12.58	7.39	–	0.98	3.77	12.27	–	0.89	3.32
Ivnyakovskoe*	53.41	15.22	6.60	0.87	6.45	4.73	1.58	0.47	0.70	9.87
Nepheline concentrate**	43.03	28.85	2.74	0.40	1.71	0.25	20.00	0.04	–	2.40

* In addition, Ivnyakovskoe clay also contains 0.10% C.

** In addition, nepheline concentrate contains 0.58% FeO.

at 430 – 475 and 520°C, a double exothermic effect corresponding to oxidation of iron to the trivalent state and to some extent sulfides is observed at 430 – 475 and 520°C. The peak intensity ratios in general are in agreement with the roentgenometric data.

In studying the possibility of using copper-nickel ore concentration wastes to make ceramic tiles, we investigated ceramic pastes of different compositions. Ermakovskoe and Ivnyakovskoe clays with different mineral compositions were used as the clay component. Ermakovskoe clay is a hydromica clay with respect to the mineral composition, and contains quartz, feldspar, and amphiboles as impurities; it is a low-dispersion clay with respect to the granulometric composition, and a moderately plastic clay with respect to the plasticity. The free quartz content is 25.1 – 36.1%. The refractoriness is 1180 – 1200°C. Ivnyakovskoe clay is a kaolinite-hydromica clay with respect to the mineral composition, contains feldspar, quartz, and nepheline as impurities; with respect to the plasticity, it is moderately plastic, with low dispersion, and a free quartz content of 10.99 – 39.38%. The refractoriness is 1210 – 1600°C. To improve sintering, nepheline concentrate, a by-product of processing apatite-nepheline ores, was added to the ceramic pastes in the amount of 10 – 20%. The chemical composition of the components of the ceramic pastes is shown in Table 1 and the compositions of the ceramic pastes are reported in Table 2.

The samples were prepared by semidry molding. The components of the batch were ground in a porcelain mill to a maximum of 5% residue on a 0.05 mm sieve. The paste obtained was moistened to a 9 – 12% moisture content. The finished molding powder was ripened for 24 h. Tiles measuring 50 × 50 × 5 mm were molded from the pastes obtained. The samples were molded in two stages.

The first stage was molding at a specific pressure of 5 MPa to remove air from the batch, and then at 21 MPa. The molded samples were dried in a desiccator for 20 min at 240°C. Firing was conducted in a Silit furnace at 1000 – 1150°C. The temperature elevation rate was 3 K/min. The samples were cooled together with the furnace. The physicomechanical properties of the samples are reported in Table 3, and an increase in the content of wastes in the batch decreased the sinterability of the ceramic pastes.

In studying the phase composition of ceramic pastes 1 and 2, it was found that it was basically represented by crystalline phases at a firing temperature of 1000 – 1050°C: quartz and feldspars. In addition to the above phases, cordierite was present in small amounts in pastes 3 and 4. Formation of cordierite in this case caused the strength to increase slightly. There was no glass phase in the phase composition of all samples. A liquid phase appeared in all pastes when the firing temperature was increased to 1100 – 1150°C, basically due to melting of albite. Quartz dissolved and anorthite formed in it. Dissolution of quartz in the liquid phase was confirmed by the decrease in the intensity of its peaks in the x-ray patterns.

When Ivnyakovskoe clay was added to the ceramic paste, the water absorption of samples 5 and 7 changed insignificantly and was within the limits of 15.2 – 12.6%. The flexural strength almost doubled in comparison to the ceramic pastes containing Ermakovskoe clay, and the clay content in the batch did not exceed 50%. According to the data from x-ray phase analysis, the phase composition of ceramic pastes 5 and 7 were basically represented by crystalline phases at a firing temperature of 1000°C: quartz, phlogopite, and cordierite. When the temperature was increased to 1050°C, a melt began to form, indicating the appearance of a glass phase. The phase composition changed — the quartz content decreased and the amount of cordierite, enstatite, and feldspars increased. At 1100°C, forsterite and hypersthene

TABLE 2

Components	Mass content, %, in composition							
	1	2	3	4	5	6	7	8
Concentration wastes	50	40	30	20	50	40	40	30
Clay:								
Ermakovskoe	40	50	60	70	–	–	–	–
Ivnyakovskoe	–	–	–	–	40	40	50	50
Nepheline concentrate	10	10	10	10	10	20	10	20

TABLE 3

Composition	Shrinkage, %, at temperature, °C				Water absorption, %, at temperature, °C				Flexural strength, MPa, at temperature, °C			
	1000	1050	1100	1150	1000	1050	1100	1150	1000	1050	1100	1150
1	0.4	0.6	0.9	1.2	16.4	15.9	15.7	15.3	2.1	2.7	3.0	3.9
2	0.3	0.6	0.7	1.0	16.0	15.8	15.1	14.9	2.4	2.8	3.1	3.9
3	0.1	0.3	0.6	0.7	15.6	15.0	14.7	14.0	2.9	3.5	4.1	4.8
4	0.2	0.3	0.5	0.9	14.3	13.8	13.2	12.9	3.7	4.4	5.0	5.6
5	1.2	1.7	3.2	3.8	15.2	15.3	12.7	11.8	6.5	7.8	12.9	19.5
6	1.1	1.5	3.2	3.2	15.4	13.7	12.3	11.8	5.1	6.9	11.0	18.4
7	1.2	1.7	3.2	3.2	15.7	15.0	13.3	12.6	5.4	9.7	10.0	17.4
8	1.0	1.8	2.7	2.7	15.4	14.5	13.5	12.5	4.9	4.9	8.1	18.0

formed, and the amount of glass phase also increased. Increasing the temperature to 1150°C caused the appearance of a large amount of liquid phase, anorthite crystallized, and the content of forsterite, hypersthene, and enstatite increased. The appearance of a large amount of liquid phase was accompanied by initial deformation of the samples. The increase in the strength of the samples when Ivnyakovskoe clay was added to the ceramic pastes was due to its chemical and mineral compositions. The high content of RO oxides in it allowed obtaining an aluminosilicate melt of low viscosity and as a result, a stronger and denser ceramic material.

To decrease the firing temperature of the tiles (samples 6 and 8), part of the wastes was replaced by nepheline concentrate. As the test results showed, incorporation of an additional amount of nepheline concentrate did not significantly alter the strength and water absorption at relatively low temperatures.

At a firing temperature of 1100°C, ceramic pastes 5 and 7 are suitable for production of facing tiles with the following characteristics: water absorption of 12.7 – 13.3%, flexural strength of 10.0 – 12.9 MPa, cold resistance of more than 25 cycles.

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